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Kinetic and Mechanistic Approach of N-Chlorosaccharin Oxidation of some Non Vicinal Poly hydroxy Alcohols

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Abstract: The kinetics of oxidation of propane-1,3-diol and butane-1,4-diol by N-chlorosaccharin was carried out in aqueous acetic acid medium. The reactions exhibit first order dependence in oxidant and the Michaelis-Menten's kinetics in substrate. Increase in the concentration of added perchloric acid increases the rate of oxidation. Addition of the reaction product, saccharin, exhibits retarding effect. Decrease in dielectric constant of the medium decreased the rate constant. Various activation parameters have been evaluated. Mechanism proposed and the derived rate law is in agreement with the observed kinetics.

Key Words: N-chlorosaacharin, polyhydroxy, iodometrically, saccharin, propane-1,3-diol.

Introduction

N-chlorosaacharin (NCSA) is a potent oxidant and has been used extensively in the kinetic and non-kinetic quantitative estimation of a few number of organic compounds[1-2]. Relatively NCSA received a little attention towards the oxidation. Kinetics involving NCSA and the mechanistic interpretations of the results are obscure. Some investigations on oxidation kinetics involving NCSA has been made with alcohol[3, 4], hydroxy acids[5, 6], acid[7], aliphatic aldehyde[8], ketones[9, 10,] benzaldehyde[11] in acidic medium. We have been interested in the kinetic and mechanistic studies of the reactions of some non vicinal poly hydroxyl alcohols. There seems to be no report on the oxidation of diols by NCSA. However several oxidations of diols are known to allow different mechanistic pathways e.g. ozone[12], PHPB[13], bromine[14], pyridinium bromochromate[15], Mn (III)[16], N-chlorocarbamate[17],cetyltrimethylammonium dichromate[18], BTMACB[19], BTMAB[20], and TFATB[21].

Hence this prompted the authors to undertake the oxidation of propane-1,3-diol (1) and butane-1,4-diol (2) by NCSA in aqueous acetic acid medium. The mechanistic aspects are discussed.

Materials and Method

Materials

The propane-1,3-diol and butane-1,4-diol were commercial products and were distilled, under reduced pressure before use. NCSA was prepared by chlorination of saccharin in alkaline medium at 0^0c and its acetic acid solution was standardized by iodometric method. Acetic acid was purified by the usual methods. All other reagents were commercial products and were purified by the usual methods.

Kinetic measurements

A thermostated water bath was used to maintain the desired temperature to within ± 0.1K. Requisite volumes of all reagents, except NCSA, were introduced into a reaction vessel and equilibrated at 308 K. A measured volume of NCSA, equilibrated separately at the same temperature, was rapidly poured into the reaction vessel. Pseudo first order conditions were maintained in each kinetic run by keeping the [diols] >> [NCSA]. To prevent any photochemical reaction, amber colored bottles were used. The progress of the reactions was monitored by periodically examining aliquots of the reaction mixture for unconsumed NCSA iodometrically[22] using starch as the indicator.

Stoichiometry & Product analysis

Product analysis was carried out under kinetic conditions. In a typical experiment, the diol (0.1 mol) and NCSA (0.01 mol) were taken in 100 ml of acetic acid-water (30%) and the mixture was allowed to stand in the dark for = 12h to ensure complete reaction. The estimation of residual NCSA in different sets showed that 1 mol of diols consumes 1 mol NCSA according to the stoichometric equation:

$$R\text{-} CH_2OH + C_6H_4COSO_2NCl + H_2O \rightarrow R\text{-}CHO + C_6H_4COSO_2NH + HCl$$

(R= HO-CH_2 CH_2 for propane-1,3-diol and HO-CH_2 CH_2 CH_2 for butane-1,4-diol)

Now remaining mixture was then treated overnight with an excess (250 ml) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm^{-3} HCl and kept in a refrigerator. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, dried, recrystallized from ethanol and weighed. The identities of products were established by comparing the m.p. of the DNP derivatives with the literature values. The end product of propane-1,3-diol is $HOCH_2CH_2CHO$ and m.p. of its DNP derivative is 131^0C and the end product of butane-1,4-diol is $HOCH_2CH_2$ CH_2CHO and m.p. of its DNP derivative is 116^0 C.

Results and Discussion

Order with respect to [N-chlorosaccharin]

The order of the reaction with respect to the concentration of NCSA is determined by studying the rate of the reaction at different initial concentrations of the NCSA. The rate constants obtained at various initial concentrations of NCSA at constant concentration of perchloric acid and diols. The plot of log (a-x) versus time (Figure 1) gave a straight line, which indicates that reaction under the chosen conditions follows pseudo first order kinetics. The order with respect to NCSA is one.

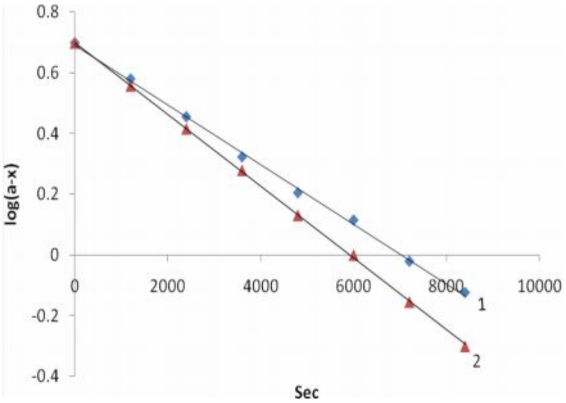


Figure 1:-The plot of log(a-x) versus time. Conditions are given in Table 1.

Order with respect to [diols]

The order in substrates was computed from the slopes of k_1 versus log [diol] plots (Figure 2) and was found to fall from 1 to zero at higher concentration of substrates. This fact shows that the reactions exhibit 1 to zero order kinetics with respect to all diols indicating Michaelis-Menten kinetics. A double reciprocal plot between k_1^{-1} versus $[diol]^{-1}$ (Figure 3) has been found to be linear with positive intercept at y-axis. This kinetic evidence of complex formation between the substrate and the oxidant, further support the first order dependence.

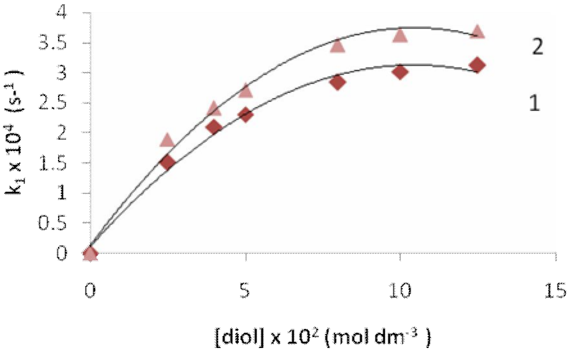


Figure 2. Dependence of k_1 on [diol]. Conditions are given in Table 1.

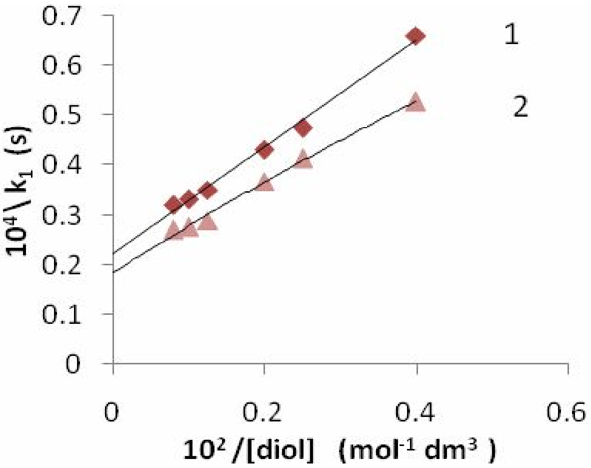


Figure 3. Double reciprocal plot depicting the dependence of the reaction rate on the concentration of diol.Conditions are given in Table 1.

Effect of variation of [H^+]

On varying perchloric acid concentration there is an increase in reaction rate (Table 1). The plot of log k_1 versus log [H^+] (Figure 4) gave a straight line with negative intercept, suggesting that acid plays a complex role in the reaction system.

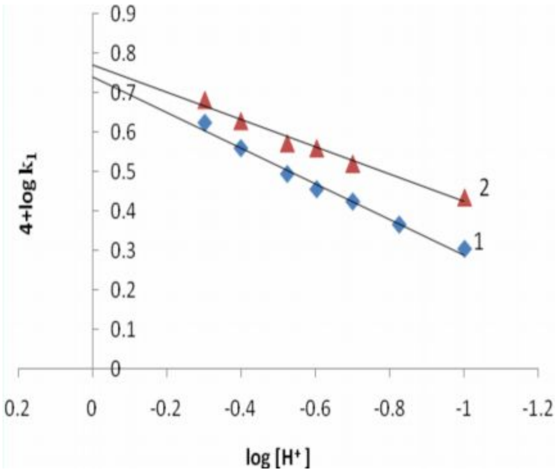


Figure 4. Dependence of k_1 on [H^+]. Conditions are given in Table 1.

Variation of ionic strength, dielectric constant and saccharin

The effect of ionic strength has been studied by varying the concentration of neutral sodium perchlorate. It was found that there is no substantial change in the reaction rate on varying the ionic strength. The effect of dielectric constant in reaction medium was studied by adding acetic acid in the reaction medium at constant concentrations of other reactants. The rate of reaction decreases by increasing the proportion of acetic acid in the solvent medium. Addition of saccharin (one of the reaction products), at constant NCSA and diol concentration, decreases the rate of reaction. This confirms that HOCl is the main oxidizing species. The retardation of reaction rate on the addition of saccharin suggests a pre-equilibrium step that involves a process in which saccharin is one of the products. If this equilibrium is involved in the oxidation process the retardation should be an inverse function of saccharin concentration, which is borne out by observation that the inverse of the rate constant gives a linear plot against [saccharin] (Figure 5).

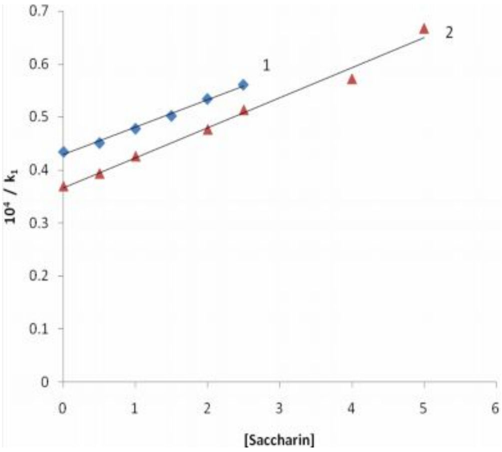


Figure 5. Plot of $1/k_1$ versus [Saccharin]. Conditions are given in Table 1.

Table 1 : Effect of variation of reactants on pseudo first order rate constant k_1 at 308K

10^2[Substrate] (mol dm^{-3})	10^3 [NCSA] (mol dm^{-3})	[H^+] (mol dm^{-3})	% HOAc - H_2O	k_1x10^4 (s^{-1})	
				Propane-1,3-diol (1)	Butane-1,4-diol (2)
2.5	2.5	0.15	30	1.513	1.898
4.0	2.5	0.15	30	2.109	2.418
5.0	2.5	0.15	30	2.310	2.717
8.0	2.5	0.15	30	2.754	3.155
10.0	2.5	0.15	30	3.026	3.439
12.5	2.5	0.15	30	3.129	3.706
5.0	1.0	0.15	30	2.331	2.711
5.0	2.0	0.15	30	2.322	2.734
5.0	4.0	0.15	30	2.340	2.725
5.0	5.0	0.15	30	2.351	2.742
5.0	2.5	0.10	30	2.012	2.421
5.0	2.5	0.20	30	2.652	3.313
5.0	2.5	0.25	30	2.851	3.628
5.0	2.5	0.30	30	3.115	3.736
5.0	2.5	0.40	30	3.622	4.255
5.0	2.5	0.50	30	4.201	4.816
5.0	2.5	0.15	10	2.712	3.501
5.0	2.5	0.15	20	2.540	5.052
5.0	2.5	0.15	40	2.037	2.303
5.0	2.5	0.15	50	1.798	2.668

Induced polymerization of acrylonitrile

The addition of acrylonitrile to the reaction mixture had no effect, indicating the absence of free radical species during the reaction. This observation further supports the participation of neutral species in rate determining step, i.e. the substrate molecule and HOCl.

Activation Parameter

Activation parameters are believed to provide useful information regarding the environment in which chemical reactions take place. The effect of temperature on the reaction of propane-1,3-diol and butane-1,4-diol with NCSA were also studied . The value of energy of activation was calculated and the values of ΔS, ΔG were also computed. These values are summarized in Table 2 along with the other parameters.

Mechanism and Rate law

The reaction is first-order with respect to NCSA. Individual kinetic runs are strictly first-order in NCSA. Further, the first-order rate coefficients do not vary with the initial concentration of the NCSA. The order with respect to the diol is one but tends to zero at higher concentration. Thus Michaelis-Menten type kinetics is observed with respect to diols. The overall mechanism therefore involves the formation of an intermediate complex before equilibrium and slow disproportination of the intermediate in the slow step. From the various relevant literatures the different probable steps involved in NCSA system may be summarized as follows:

$$\text{NCSA} + H_2O \overset{K_1}{\rightleftharpoons} \text{HOCl} + \text{Saccharin(S)}\ldots (1)$$

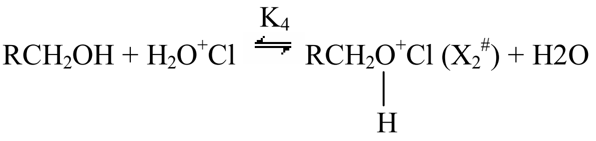
$$\text{HOCl} + H^+ \overset{K_2}{\rightleftharpoons} H_2O^+Cl \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(2)$$

$$\text{NCSA} + H^+ \rightleftharpoons \text{NCSAH}^+ \ldots\ldots\ldots\ldots\ldots\ldots\ldots..(3)$$

$$\text{NCSAH}^+ + H_2O \rightleftharpoons H_2O^+Cl + \text{Saccharin} \ldots(4)$$

Therefore HOCl, H_2O^+Cl and $NCSAH^+$ are the possible oxidizing species in acidic medium. The retardation of reaction rate with the added saccharin to the reaction mixture rules out the possibility of $NCSAH^+$ as the reacting species. The reaction is acid dependent and it is justified to assume analogous to H_2O^+Br[15], H_2O^+Cl as the reacting species of the choice existing in aqueous acetic acid medium. At the same time experimental evidence indicates HOCl is also a oxidizing species.This leads to the postulation of the following overall mechanism and rule law.

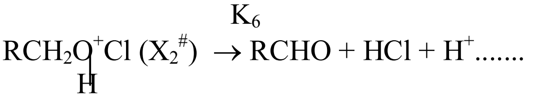
$$RCH_2OH + HOCl \overset{K_3}{\rightleftharpoons} RCH_2OCl\ (X_1^{\#}) + H_2O \ldots(5)$$



$$RCH_2OH + H_2O^+Cl \overset{K_4}{\rightleftharpoons} \underset{\displaystyle H}{RCH_2O^+Cl}\ (X_2^{\#}) + H2O$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

$$RCH_2OCl\ (X_1^{\#}) \overset{K_5}{\rightarrow} RCHO + HCl \ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$



$$\underset{\displaystyle H}{RCH_2O^+Cl}\ (X_2^{\#}) \overset{K_6}{\rightarrow} RCHO + HCl + H^+ \ldots\ldots\ldots \quad (8)$$

(R= HO-CH_2 CH_2 for propane-1,3-diol and HO-CH_2 CH_2 CH_2 for butane-1,4-diol)

On the basis of the aforementioned steps involved in the proposed mechanism and at steady state approximation condition, the final rate law is derived as;

$$k_1 = \frac{K_1\ [diol]\ (\ K_3\ K_5 + K_2\ K_4\ K_6\ [H^+]\ )}{[S] + K_1\ (1 + K_3\ [diol]\ )} \ldots\ldots(9)$$

On comparing the values of rate constants obtained in the case of two diol viz. Propane-1,3-diol and butane-1,4-diol; it is quite clear that the rate of complex formation of hypochlorite ester is in the following order, i.e.,

butane-1,4-diol > propane-1,3-diol

The above rate law equation explain fully well the experimental results obtained for the first order kinetics, the plot of 1/[rate] versus 1/[substrate] give rise a straight line with positive intercept which gives the value of k and furnishes an evidence for the formation of complex between substrate and reactive species of the oxidant. Thus in both the cases the rate determining step involves C-H bond fission. Thus degree of agreement again shows the validity of rate law and hence confirms the proposed reaction mechanism. The E_a value is the highest for the slowest for the reaction showing that reactions are enthalpy controlled.

Conclusion

Kinetic studies demonstrate that the complex between, substrate and oxidant decomposes in a slow rate determining step to give product. The experimental stoichiometry is in good agreement. First order to oxidant and fractional order to substrate at higher concentration is supported by derived rate law. The rate of oxidation of diols was found to be in the order of butane-1,4-diol > propane-1,3-diol.

Table 2. Thermodynamic parameters of diol-NCSA system

Diols	Ea (kJ mol^{-1})	A (s^{-1})	ΔH* (kJ mol^{-1})	ΔG* (kJ mol^{-1})	-ΔS* (JK^{-1} mol^{-1})
Propane-1,3-diol	63.695	1054720	42.1	89.180	155.5
Butane-1,4-diol	57.438	1047199	37.1	88.345	169.3

References

[1] Chattaway, F.D. J.Chem.Soc., **1905**, 87, 1884.

[2] Bacchawat, J.M.; Mathur, N.C. Indian J.Chem., **1971**, 9, 1335.

[3] Vijay Mohan, K.; Raghunath Rao, P.; Sundaram, E.V. Proc.N.Acad.Sc.India, **1988**, 58(A),137.

[4] Khan, M.U.; Tiwari, R.K.; Verma, J.K.; Gupta, H.D. Oxid.Commun., **1997**, 20**,** (1) , 124.

[5] Khan, M.U.; Sharma, V.K.; Verma, J.K.; Dwivedi, H.P. Oxid. Commun., **1991**,14**,** (1), 60.

[6] Khan,M.U.;Verma, J.K.; Singh, V.R.; Dwivedi, H.P. Oxid. Commun., **1993**, 16 (3), 235.

[7] Khan, M.U.; Nigam, S.K.; Nigam, A.; Verma, J.K.; Chauhan, R.P.S. Oxid. Commun., **1995**, 18 (3), 304.

[8] Khan, M.U.; Verma, J.K.; Parihar, S.S..; Dwivedi, H.P. Oxid. Commun., **1998**,21 (3), 362.

[9] Khan,S.; Khan,M.U.; Singh,S.K.; Gupta,H.D.; Singh, P.K. Asian J. Chem., **2003**,15 (2), 595.

[10] Khan,S.;Nigam,S.K.; Khan,M.U.; Dwivedi,H.P.; Singh, P.K. Asian J. Chem., **2004**, 16 (2), 751.

[11]Nigam,S.K.;Khan,M.U.;Tiwari, S.; Dwivedi,H.P.; Singh, P.K. Asian J. Chem., **2004**, 16 (2), 362.

[12]Zimin,Y.S.; Trikhanova,N.V.; Shamsuldinov,R.R.; Komissarov,V.D. Reaction Kinetics and Catalysis Letters; **1999**,68, (2), 237.

[13] Mathur, D.; Sharma, P.K.; Banerji, K.K. J.Chem. Sci.: **1995**,107, (2),133.

[14] Sharma, V.; Sharma, P.K.; Banerji, K.K. Proc.Ind.Acad. Sci. **1998**,110(1); 65.

[15] Rao, P.S.C.; Suri, D.; Kothari, S.; Banerji, K.K. Int. J.Chemical Kinetics **1999**, 30 (4) ; 285.

[16]Chary,V.B.; Rao,M.A. Oxid. Commun.,**2002**,25**,** (3), 432.

[17]Grover,A.;Varshney,S.;Banerji K.K.; J.Chem. Soc., Perkin Transcation 2 **1994**, 629.

[18] Patel, S.;Sung, D.D.;Mishra, B.K.; Indian J. Chem. **2008**, 47A, 1218.

[19] Bhatt, M.; Sharma, P.K.; Banerji, K.K. Indian J. Chem. **2002**, 41(4), 826.

[20] Goswami,G.; Kothari, S.; Banerji, K.K. Proc.Ind.Acad. Sci. **2001**,113(1); 43.

[21] Gosain, J.; Sharma, P.K.; Proc.Ind.Acad. Sci. **2003**,115(2); 135.

[22] Barkat,M.Z.; Wahab,A. Analyt. Chem., **1954**,26; 1973.

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